POROUS $LiCoO_2$ FILM AS A BATTERY CATHODE

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Cobalt oxide in thin film form can be used in several applications, as $LiCoO_2$ cathodes in microbatteries, or Co_3O_4 films in electrocatalysis [1] and in electrochromic devices [2]. $LiCoO_2$ has been synthesised using solid-state reaction which requires long-range diffusion of the reactants and high temperature (> 900 ^oC). In this work, we adopted two different routes to obtain this oxide: the sol gel process and the template approach.

The gel precursor was formed at 160 ^oC by mixing $Co(CH_3COO)_2$ and $LiCH_3COO$ (Co/Li = 1:4 atom ratio) with citric acid in ethylene glycol solution. Conventional thin films (CF) were obtained by spin-coated on ITO glass plates followed by annealing at 500 ^oC in air.

The same oxide film with porous morphology [3] (PF) was obtained using cellulose acetate membrane (CA) as template it is stable in organic media and undergo pyrolysis on heating. A 10 % wt. of cellulose acetate PW 5000 solution in acetic acid was spin-coated on ITO glass. Phase separation was promoted by immediate immersion in a gel precursor. The pink hybrid material was then heated at 450 ^oC in air.

Endothermic peak in the DTA curve (Figure 1) at about 200 ^oC was attributed to the removal of ethylene glycol in the gel precursor in both films. A single phase of $LiCoO_2$ is only formed when the CA template was used (exothermic peak at 450 ^oC), indicating that a more homogeneous oxide is obtained by template method (curve b). In the case of gel precursor (curve a), the presence of a double exothermic peak at 440 and 478 ^oC indicated the formation of mixed oxide. The complete pyrolysis of the cellulose acetate membrane occurs at a higher temperature than crystallisation process of oxide.

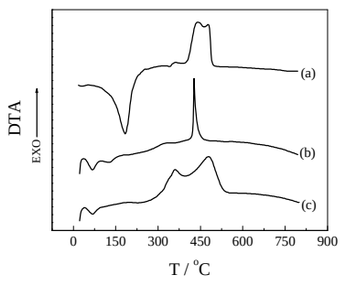

Fig. 1 – *Differential thermal analyses of gel precursor (a), gel precursor/cellulose acetate membrane (b) and cellulose acetate membrane (c), at a heating rate of 5 $^oC.min^{-1}$.*

Figure 2 presents the cyclic voltammetric profiles for both materials. The porous film shows anodic (4.0 V) / cathodic (3.8 and 3.2 V) peaks corresponding to Li deintercalation / intercalation process. The corresponding peaks to conventional film are not so well defined.

Figure 3 presents the discharge plot. The initial open circuit potential was 3.35 V for both films. The porous film delivered approximately 65 $mC.cm^{-2}$ while the conventional electrode showed 50 $mC.cm^{-2}$. In the case of porous film a wide plateau near 3.4 V is observed, indicating a phase transition.

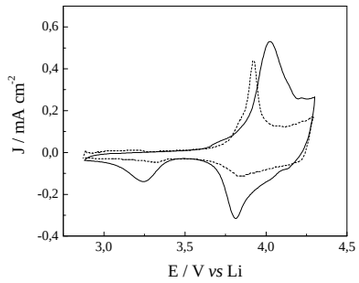

Fig. 2 – *Steady state cyclic voltammogram of $LiCoO_2$ film (dashed line) and $LiCoO_2$ porous film (solid line) in PC/EC/1.0 mol.l^{-1} $LiClO_4$; at 5 mV.s^{-1}.*

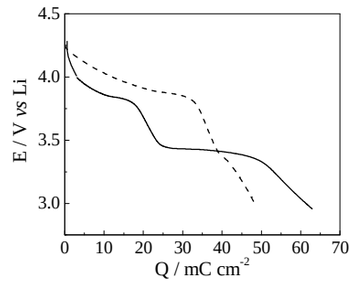

Fig. 3 – *Discharge curve of $LiCoO_2$ film (dashed line) and $LiCoO_2$ porous film(solid line); i = ± 5 μA.*

The impedance spectra are shown in Figure 4. As in the OCP as 4.2 V (full charged state) the same profile was observed, that is, the conventional film impedance is one order of magnitude higher than porous film. This behavior is due to higher porosity of PF that makes the lithium transfer process easier.

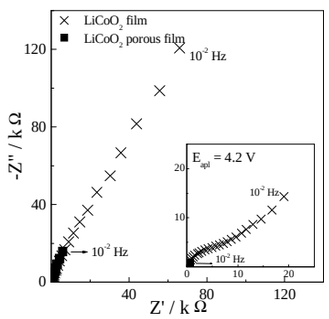

Fig. 4 – *Nyquist diagram at OCP potential (3.45 V) and at 4.2 V (full charged state) in zoom part. Perturbation amplitude: 0.01 V and frequency range from 10^{-2} to 10^5 Hz.*

The porous morphology of $LiCoO_2$ films was obtained by using the template approach. All techniques employed to characterize this material show the availability of this purpose.

Acknowledgements

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